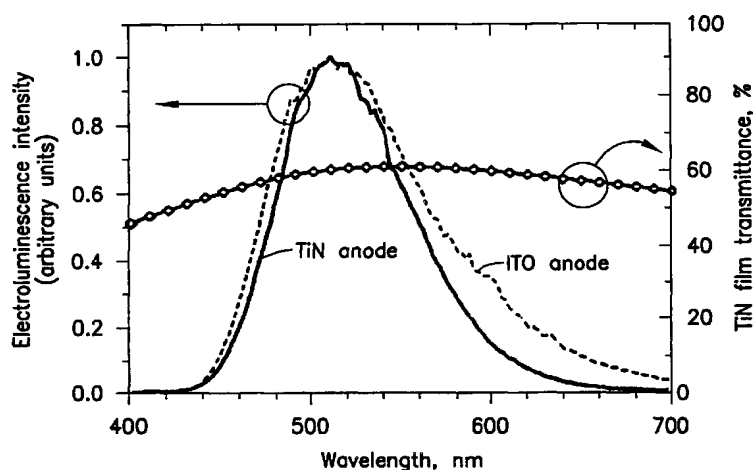




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B32B 19/00, H01J 1/62		A1	(11) International Publication Number: WO 00/69625
			(43) International Publication Date: 23 November 2000 (23.11.00)
(21) International Application Number: PCT/US00/12737 (22) International Filing Date: 10 May 2000 (10.05.00) (30) Priority Data: 60/134,242 13 May 1999 (13.05.99) US (71) Applicant: THE UNIVERSITY OF SOUTHERN CALIFORNIA [US/US]; Suite 313, 3716 South Hope Street, Los Angeles, CA 90007-4344 (US). (72) Inventors: THOMPSON, Mark, E.; 4447 Pepper Creek Way, Anaheim, CA 92807 (US). ADAMOVICH, Vadim; Apartment 6, 1103 W. 30th Street, Los Angeles, CA 90007 (US). SHOUSTIKOV, Andrei; Apartment 29, 372 Monterey Road, South Pasadena, CA 91030 (US). (74) Agents: MEAGHER, Thomas, F. et al.; Kenyon & Kenyon, One Broadway, New York, NY 10004 (US).		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	

(54) Title: TITANIUM NITRIDE ANODE FOR USE IN ORGANIC LIGHT EMITTING DEVICES



(57) Abstract

An organic light emitting device (OLED), including a substrate (10), a conductive nitride electrode (11), an organic film (12), and a second conductive electrode (13). The conductive nitride films (11) can be transparent or opaque depending on their thickness. The OLEDs provide high brightness and efficiency and can be incorporated into electronic devices, including computers, monitors, televisions, large area wall screens, theater screens, stadium screens, billboards, signs, vehicles, printers, telecommunication devices, and telephones.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITANIUM NITRIDE ANODE FOR USE IN ORGANIC LIGHT EMITTING DEVICES

5 Field of the Invention

This invention relates to the use of conductive nitrides, particularly TiN, as electrode material in organic light emitting devices.

Background of the Invention

10 Organic light emitting devices (OLEDs), which make use of thin film materials that emit light when excited by electric current, are becoming an increasingly popular form of flat panel display technology for applications such as television sets, computer terminals, telecommunications equipment and a host of other applications. There are presently three predominant types of OLED construction: the “double heterostructure” (DH) OLED, the
15 “single heterostructure” (SH) OLED, and the single layer polymer OLED.

In the DH OLED, as shown in Fig. 1A, a substrate layer of glass 10 is coated by a thin layer of indium-tin-oxide (ITO) 11. Next, a thin (100-500 Å) organic hole transporting layer (HTL) 12 is deposited on ITO layer 11. Deposited on the surface of HTL 12 is a thin (typically, 50Å - 500Å) emission layer (EL) 13. The EL 13 provides the site for electrons

injected from a 100-500Å thick electron transporting layer 14 (ETL) to recombine with holes from the HTL 12. Examples of prior art ETL, EL and HTL materials are disclosed in U.S. Patent No. 5,294,870, the disclosure of which is incorporated herein by reference.

Often, the EL 13 is doped with a highly fluorescent dye to tune color and increase the electroluminescent efficiency of the OLED. The device as shown in Fig. 1A is completed by depositing metal contacts 15, 16 and top electrode 17. Contacts 15 and 16 are typically fabricated from indium or Ti/Pt/Au. Electrode 17 is often a dual layer structure consisting of an alloy such as Mg/Ag 17' directly contacting the organic ETL 14, and a thick, high work function metal layer 17'' such as gold (Au) or silver (Ag) on the Mg/Ag. The thick metal 17'' is opaque. When proper bias voltage is applied between top electrode 17 and contacts 15 and 16, light emission occurs from emissive layer 13 through the glass substrate 10. An LED device of Fig. 1A typically has luminescent external quantum efficiencies of from 0.05% to 2% depending on the color of emission and the device structure.

The (SH) OLED, as shown in Fig. 1B, makes use of multi-functional layer 13' to serve as both EL and ETL. One limitation of the device of Fig. 1B is that the multi-functional layer 13' must have good electron transport capability.

A single layer polymer OLED is shown in Fig. 1C. As shown, this device includes a glass substrate 1 coated by a thin ITO layer 3. A thin organic layer 5 of spin-coated polymer, for example, is formed over ITO layer 3, and provides all of the functions of the HTL, ETL, and EL layers of the previously described devices. A metal electrode layer 6 is formed over organic layer 5. The metal is typically Mg or other conventionally used low work function metal.

The choice of materials to be used in OLEDs is based on several criteria. For

example, the anode in a conventional OLED must have good optical transparency, good electrical conductivity and chemical stability. Indium tin oxide (ITO) meets these criteria and is the most widely used anode material in OLEDs. ITO films combine high transparency ($\approx 90\%$) with low resistivity ($1 \times 10^{-3} - 7 \times 10^{-5} \Omega \cdot \text{cm}$) and can be prepared by a variety of methods including sputtering, chemical vapor deposition (CVD) and sol-gel techniques.

However, OLEDs using ITO films do have a few areas which could be improved upon. First, the work function of ITO (4.4-4.7 eV, based on ultraviolet photoemission spectroscopy measurements) lies near the HOMO levels of typical OLED hole transporting or injecting materials, thus leading to a barrier for hole injection into organic material. Second, an OLED's stability and efficiency strongly depend on the nature of the anode/organic film interface. Therefore, any changes in this interface over time will destabilize the OLED. For example, one cause of long term OLED degradation involves the diffusion of metal ions or oxygen from the ITO film into the organic film. Finally, another issue arising from the use of an ITO anode is the tendency of SnO_x and InO_x islands to form through reorganization of the ITO film over time.

Therefore, although ITO electrodes have been used with many different organic materials, additional OLED anode materials are needed.

Summary of the Invention

The present invention provides organic light emitting devices, including polymer, (e.g. single and multi-layer), single heterostructure, and double heterostructure, which use conductive nitride films as anode material. These anode layers can be transparent or opaque and can be used in OLEDs with transparent cathodes. In addition, the formed OLEDs with TiN or TiN/ITO anode layers can be used to form stacked OLEDs.

The OLEDs of the present invention can be incorporated in electronic devices, including computers, monitors, televisions, large area wall screens, theater screens, stadium screens, billboards, signs, vehicles, printers, telecommunication devices, and telephones.

One embodiment of the present invention comprises forming a thin TiN film on a glass substrate and then forming an OLED using the TiN film as an anode layer. Another embodiment of the present invention uses a multi-layered anode of TiN on top of ITO in forming an OLED.

Brief Description of the Drawings

Fig. 1A is a cross sectional view of a typical organic double heterostructure light emitting device (OLED) according to the prior art.

Fig. 1B is a cross sectional view of a typical organic single heterostructure light emitting device (LED) according to the prior art.

Fig. 1C is a cross sectional view of a known single layer polymer LED structure according to the prior art.

Fig. 2 is a graph of TiN film transmittance versus thickness in angstroms.

Fig. 3 is a current-voltage plot of TiN and ITO anode OLEDs.

Fig. 4 is a graph of electroluminescence of TiN and ITO anode OLEDs and the transmittance of a TiN film.

Fig. 5 is a current-voltage plot of TiN/ITO and standard ITO anode OLEDs.

Detailed Description

The present invention provides light emitting devices that use conductive nitrides as anode material. The present invention's conductive nitride anodes can be transparent or opaque depending on the thickness of the anode film/layer. In addition, these conductive

nitride anodes can be used with transparent cathodes.

While the illustrative embodiments below speak in terms of titanium nitride, it should be understood that any conductive nitride may be used. Furthermore, while the illustrative embodiments below speak in terms of single heterostructure OLEDs, it should be understood that any type of OLED (e.g. polymer (single and multi-layered), single heterostructure, or double heterostructure) may be formed.

First Embodiment

In a first embodiment of the present invention, small molecule based OLEDs were prepared on glass substrates having varying TiN thickness layers. OLEDs with ITO anodes were also made for comparison. In each experiment two devices were made at the same time, (*i.e.*, the organic and metal films were deposited on both substrates at the same time) one ITO/ α -NPD/Alq₃/Mg-Ag device used as a reference device and one TiN/ α -NPD/Alq₃/Mg-Ag device. The purpose of making the devices at the same time was so that the only difference between the devices would be the anode layers. The OLEDs consisted of a 400 Å hole transporting layer (α -NPD), a 500 Å electron transporting layer (Alq₃) and a 10:1 Mg/Ag cathode of 800 - 1,000 Å thus forming either TiN/NPD/Alq₃/Mg-Ag or ITO/NPD/Alq₃/Mg-Ag. The organic materials were deposited as uniform sheets, while the Mg/Ag cathodes were deposited as 1 mm diameter dots.

The TiN films were prepared by atmospheric pressure metalorganic CVD from tetrakis(dimethylamido)titanium (TDMAT) [(CH₃)₂N]₄Ti and ammonia and deposited onto glass substrates. The TiN film preparation process used is similar to the one reported by Joshua N. Musher and Roy G. Gordon in *J. Mater. Res.*, 1996, 11(4) 736-744.

To form the TiN films, TDMAT (technical grade) from Aldrich Chemical Company

was purified by vacuum distillation. Semiconductor purity ammonia was mixed with ultra high purity (UHP) nitrogen in a ratio of 1.2:1 (by volume) and fed into a laminar flow CVD reactor (4 inch diameter tube furnace) heated to 150°C. The glass substrate was mounted on a surface heater placed in the center of the CVD furnace and heated to between 300 and 400°C. UHP nitrogen was bubbled through liquid TDMAT at 65°C and the resulting TDMAT saturated nitrogen stream was injected into the CVD reactor through a nozzle near the substrate. During the deposition, the nozzle was moved along the substrate surface, leading to uniform films roughly 2 cm x 2 cm in area. The deposition time to produce a 50-200 Å TiN film was no more than 2 minutes.

The compositions of the obtained TiN films were analyzed by x-ray diffraction, TEM Energy Dispersive X-ray analysis (EDX), and Auger Electron Spectroscopy (AES). The thickness of the films was determined by ellipsometry using 632 nm laser light ($n = 1.5$ and $k = 1.75$ for TiN at this wavelength, P.J. Martin, R.P. Netterfield, and W.G. Sainty. Vacuum, 1982, 32(6) 359-362), AES depth profile, and light absorption. SEM was also used to determine the thickness of the TiN film. The uniformity and roughness of the films were checked by SEM and atomic force microscopy (AFM). In addition, the electrical resistivity of the films was measured by a four-point probe method.

The TiN films prepared by atmospheric pressure metalorganic CVD had a silver-bluish color in reflected light and ranged from light brown to greenish in color in transmitted light (transmittance 80 - 50% for films of 50 - 200 Å). The TiN films were near stoichiometric, containing a small amount of oxygen (approximately 5% or less) and carbon (approximately 5% or less) based on EDX and AES. The x-ray diffraction pattern of the TiN samples was consistent with that reported for $Ti_{1.0}N_{1.0}$ and the resistivity of these films ranged from

approximately 400-500 $\mu\Omega$ -cm.

Sheet resistances were measured for the TiN films and varied depending on film thickness as shown in Table 1. TiN films of 900-1000 Å thickness typically have sheet resistances of approximately 40 Ω/\square (ohms per dimensionless value), which is lower than ITO films of the same thickness.

The ITO on glass (100 Ω/\square) and TiN on glass substrates were first cleaned in boiling 1,1,1-trichloroethane and then in acetone for 3-4 minutes followed by sonication in isopropanol for 2 minutes. After this cleaning procedure, the substrates were dried under a N_2 flow.

The background pressure in the deposition system prior to OLED fabrication was normally 6×10^{-6} Torr, and the pressure during film deposition was between 6×10^{-6} and 1×10^{-5} Torr. The compounds used for fabrication of the OLEDs were evaporated from resistively heated tantalum boats onto the substrates at room temperature. 4,4'-Di(phenyl- α -naphthylamino)biphenyl (α -NPD) and aluminum-tris(8-quinoloxide) (Alq_3) were deposited successively at a rate of 0.8-2 Å/sec to give film thicknesses of approximately 400 Å and 500 Å, respectively. After deposition of the organic films, the chamber was vented and a shadow mask was put onto the substrates to pattern the cathodes as 1 mm diameter dots. Magnesium and silver were then co-deposited at a rate of 2 Å/s for magnesium and 0.15-0.2 Å/s for silver. The corresponding ratio of Mg:Ag was approximately 10:1. The thickness of the cathode layer was approximately 800-1000 Å.

The devices were characterized in air within 4 h of fabrication. Current-voltage measurements were made with a Keithley source meter (model 2400). Light intensity was measured using a Newport model 1835 optical power meter and silicon radiometer. EL

spectra were measured with a Photon Technology International fluorimeter. Optical transmittance at 632 nm was also measured using a HeNe laser and photodetector.

The TiN thickness for each OLED tested was determined using the film absorptivity ($1.5 \times 10^5 \text{ cm}^{-1}$) and the transmittance of the TiN film immediately adjacent to the OLED, measured using a 632 nm laser and photodetector. The data for several devices are given in Table 1. The anode thicknesses for all of the TiN devices were significantly less than that of the ITO devices.

The usable range of TiN thickness is approximately 40-180 Å and the sheet resistance depending on thickness, ranges from approximately 200 to 1500 Ω/\square . The light output of the devices can reach 10,000 Cd/m^2 or more.

Figure 3 shows the current-voltage characteristics of some of the TiN OLEDs including an IV curve for one of the ITO device. The differences in the I-V characteristics of the individual TiN devices are attributed to the different thicknesses of the TiN films used in each device. This is seen in slightly higher drive voltages required for the TiN devices. For example, the drive voltage required to achieve 100 Cd/m^2 for the TiN OLEDs was typically 1 Volt higher than for the ITO anode OLEDs, (compare 10-10.5, and 9-9.5 V, respectively). These voltages are typically for OLEDs fabricated with 400 Å of NPD and 500 Å of Alq_3 .

Device	Anode Thickness Å	Anode Sheet Resistance (Ω/\square)	External quantum efficiency at 100 Cd/m ² , % ^a	External quantum efficiency, %	I, mA	Light output, Cd/m ²	Corrected External quantum efficiency, %
TiN-a1	97	380	0.32	0.36	0.63	2,750	0.60
TiN-a2	56	700	0.51	0.41	0.69	3,440	0.63
TiN-a3	37	1,200	0.38	0.43	0.56	2,970	0.61
TiN-a5	ca. 25	160,000	0.17	0.44	0.14	762	0.52
TiN-b6	93	850	0.22	0.27	0.49	1,600	0.42
TiN-b7	185	260	0.18	0.21	0.40	1,000	0.45
TiN-b8	230	190	--	--	0.61	--	--
ITO-1	2,000	100	0.16	0.33	1.86	7,420	--
ITO-2	2,000	100	0.23	0.35	2.29	9,640	--

TABLE 1

^a Voltages for TiN OLEDs were typically between 10-10.5 Volts, while ITO anode devices were 9-9.5 Volts.

Table 1 indicates that the quantum efficiencies for OLEDs with TiN < 100 Å are better than the ITO devices. In Table 1, the quantum efficiencies for each device are listed both at a set brightness of 100 Cd/m² and at a fairly high brightness for each device (potential of 15 Volts for all devices). Table 1 shows that as the TiN films are made thicker the current-voltage characteristics improve, but the external quantum efficiencies decrease. The decreasing quantum efficiency is due to the increasing optical density of the anode as the TiN is made thicker, absorbing more of the electroluminescence. The transmittance spectrum of TiN is relatively flat, showing a maximum transmittance in the green part of the spectrum as

shown in Figure 4. The electroluminescence spectra of a TiN anode OLED and an ITO anode OLED are also shown in Figure 4. Both spectra are consistent with exclusive emission from the Alq₃ layer, with very little difference in line shape and λ_{max} . The transmittance of the TiN films at 632 nm as a function of TiN film thickness is given in Figure 2. The value of absorptivity determined from this data is $1.5 \times 10^5 \text{ cm}^{-1}$. TiN films thicker than 200 Å typically have too high an optical density to make good transparent anodes for OLED applications.

The external quantum efficiencies can be corrected for the TiN anode absorption previously discussed. The corrected external quantum efficiency values shown in Table 1 were obtained by taking into account the absorption losses of light in the TiN films. The value of the external quantum efficiency of the devices with a TiN anode was divided by the coefficient α calculated as:

$$\alpha = \frac{\int (EI_{\text{TiN}} \times T_{\text{TiN}}) d\lambda}{\int (EI_{\text{std}} \times T_{\text{std}}) d\lambda}$$

where

EI – electroluminescence intensity

T -- optical transmittance

TiN – device with TiN (or TiN/ITO) anode

std – standard reference device with ITO anode (transmittance assumed is equal 1).

Therefore, α depends on the TiN's film thickness, for example, for a 185 Å TiN film, α would be 0.46.

The corrected quantum efficiency values for TiN OLEDs are significantly higher than

for ITO based devices, averaging 0.6% for the TiN-bx set of devices, demonstrating that TiN can efficiently inject holes into standard organic hole transporting materials.

Second Embodiment

In a second embodiment of the present invention, TiN thin films are deposited onto ITO films formed on glass substrates. The multi-layered stack (TiN/ITO) is then used as anode material for forming OLEDs. While this embodiment of the present invention describes using ITO as part of the multi-layered anode, it should be recognized that TiN or any conductive nitride could be deposited on any transparent electrode film to form this multi-layered anode material.

Titanium nitride thin films on top of ITO used as anodes for OLEDs were prepared by atmospheric pressure metalorganic CVD from TDMAT and ammonia. The process described below for preparation of TiN is similar to Embodiment 1. TDMAT, technical grade, from Aldrich Chemical Company was purified by vacuum distillation. Semiconductor purity ammonia was mixed with UHP nitrogen in a ratio of 1.2:1 (by volume) and fed into a laminar flow CVD reactor (4 inch diameter tube furnace) heated to 150°C. The substrate (ITO coated glass with sheet resistance 100/□) was mounted on a surface heater placed in the center of the CVD furnace and heated to between 370 and 400°C. UHP nitrogen was bubbled through liquid TDMAT at 65-75°C and the resulting TDMAT saturated nitrogen stream was injected into the CVD reactor through a nozzle near the substrate. During the deposition the nozzle was moved along the substrate surface, leading to uniform films roughly 2 cm x 2 cm in area. Film thickness was controlled by the deposition time. The time to deposit a 50 Å TiN film was no more than 1 minute.

The composition, thickness, uniformity, roughness, and electrical resistivity were

determined and checked in the same manner as described in Embodiment 1.

The resulting TiN film thicknesses ranged from approximately 20 to 350 Å and had a silver-bluish color in reflected light and ranged from light brown to greenish in color in transmitted light (transmittance 80 -50% for films of 50 - 200 Å).

5 The present embodiment involved a 20-50 Å film of TiN on ITO. The TiN was near stoichiometric, containing a small amount of oxygen and carbon (ca. 5% or less) based on EDX and AES. The x-ray diffraction pattern of the TiN samples was consistent with that reported for $Ti_{1.0}N_{1.0}$. The resistivity of a TiN film of this thickness alone was 400-500 $\mu\Omega\cdot\text{cm}$. The sheet resistances measured for the TiN on ITO films varied depending on the
10 TiN film thickness from 75 to 85 Ω/\square . The ITO on glass (100 Ω/\square) and TiN on ITO on glass substrates were cleaned in boiling trichloroethylene, acetone and isopropanol as described in Embodiment 1.

OLEDs were then prepared as described in Embodiment 1 with both 1 and 2 mm cathodes. In each experiment two devices were made at the same time. One of them was an
15 ITO/NPD/ Alq_3 /Mg-Ag/Ag device used as a reference and the other one was a ITO/TiN/NPD/ Alq_3 /Mg-Ag/Ag device. Table 2 shows experimental data for TiN/ITO anode OLEDs at a brightness of approximately 100 cd/m^2 . The quantum efficiencies for both the ITO and TiN/ITO OLEDs are very similar, consistent with the thin TiN films having little impact on the electronic structure of the device. The voltage offset observed between the ITO
20 and TiN/ITO devices is roughly 1 V, as shown in Figure 5. This offset is significantly less than the 5-6 V offset that is observed for ITO versus TiN OLEDs.

diam 2 mm					
Device #	V	I, mA	Q.E., %	Light, nW	Cd/m2
c8	8.6	0.10	0.35	804	101.4
c7	9.2	0.09	0.39	801	101.0
c5	8.8	0.12	0.31	860	108.4
c4	9.0	0.08	0.43	840	105.9
ITO std. C3	7.0	0.12	0.28	790	99.6
ITO std. C4	7.2	0.11	0.32	798	100.6
diam 1 mm					
Device #	V	I, mA	Q.E., %	Light, nW	Cd/m2
b8	8.2	0.02	0.35	193	97.5
b6	9.4	0.03	0.33	228	115.2
b5	9.4	0.05	0.18	216	109.1
ITO std. E2	7.0	0.03	0.33	209	105.6
ITO std. D2	8.0	0.03	0.32	235	118.7
ITO std. D3	7.8	0.03	0.35	212	107.1

TABLE 2

Third Embodiment

In addition to the single OLED structure of the first and second embodiments, another embodiment of the invention comprises stacking at least two OLEDs to form a multi-layered stacked OLED. The structure of this multi-stacked OLED is similar to those described in U.S. Patent No. 5,703,436, hereby incorporated by reference. The following illustrative example speaks in terms of OLEDs described in the first embodiment of the current disclosure, but it should be understood that any of the OLEDs including a TiN anode structure may be used to form the stacked OLEDs of the present embodiment.

A multi-stacked OLED of this embodiment includes a substrate, a first OLED, including a TiN layer formed over the substrate, an organic emissive structure, including α -NPD and Alq₃, formed over the TiN layer, and a Mg-Ag layer formed over the organic emissive structure, and a second OLED of the same structure except the TiN layer is formed over the Mg-Ag layer of the first OLED. In addition to stacking two OLEDs of the present invention, a third OLED including a TiN anode could be added to this structure. It should also be noted that different types of OLEDs could be stacked, e.g. a combination of OLEDs with TiN anodes and without TiN anodes.

Fourth Embodiment

Another embodiment of the present invention includes forming TiN anode OLEDs with substantially transparent cathodes. In this embodiment the cathode material is substantially transparent and depending on the desired use for the OLED, the TiN anode could be transparent or opaque (greater than approximately 500 Å). As incorporated above, U.S. Patent No. 5,703,436 describes a process for forming transparent Mg-Ag cathodes.

Nitride	Homogeneity range ^a 1-x at 1700 K	Structure (Bravais lattice)	Lattice parameter (room temp.) (nm)	Density (g cm ⁻³)	Color	Microhardness (room temp.) (GPa)	Melting point ^c (K)	Heat conduct. ^b room temp. (W m ⁻¹ K ⁻¹)	Thermal exp. coefficient at 1000 K (10 ⁻⁶ K ⁻¹) comp. (1-x)	Electr. resistance (room temp.) ^b ($\mu\Omega$ cm)	Supercond. transition temp. T _c (K) comp. (1-x)
TiN _{1-x}	0.50 1.00	fcc	0.4215 0.4242	- 5.39 ^a	Metallic gray Golden yellow	23 17	- 3320	- 29	- 9.4 (0.95)	- 25	<1 5.8
ZrN _{1-x}	0.54 1.00	fcc	0.4585 ~0.4570	- 7.32 ^a	Light yellow Light yellow	- 15	- 3250	- 11	- 8.2-9.1 (0.92)	- 21	- 10.47
HfN _{1-x}	0.70 1.06	fcc	0.4523 0.4514	- 13.83 ^a	Light yellow Dark yellow	13.9 (0.94) 15.9 (1.00)	- 3600	- 11	- 8.6	- 33	8.7 (0.85) 6.92
VN _{1-x}	0.70 1.00	fcc	0.4060 0.4138	6.05 6.04	Brown yellow Brown yellow	13.0 5.7	- 2620	- 11	11.0 10.8	- 65	2.7 (0.76) 8.9
NbN _{1-x}	0.84 1.00	fcc	0.4380 0.4392	8.24 (0.92) 8.18 (0.95)	Pale yellow Pale yellow	13.0 11.0	- - ^d	- 3.8	9.5 (0.92) 10.2 (0.95)	- 60	13.8 (-0.84) 17.2
TaN _{1-x}	0.72 (2200 K) 1.00	fcc	0.4345 0.4328	- 15.9 ^a	- Gray yellow	- 32	- - ^d	- -	- 8.0	- -	- 8.9 (0.94)
TaN	>0.99 1.00	hex	^a 0.5190 ^c 0.2911	14.3 -	Dark gray -	11 -	- - ^d	- 9.54	- -	- 128	- -
CrN	>0.97 ^a 1.00	fcc	0.4148 -	6.14 -	Gray brown -	11 -	- 1300 ^d	11.7 -	2.3 -	- 640	- -
Cr ₂ N	0.31 ^a 0.50	hcp	^a 0.4750 ^a ^c 0.4430 ^a ^a 0.4796 ^c 0.4470	6.51 -	Gray -	12 ^a 14 ^b	- 1800	- -	- -	- 81	- -
MoN _{1-x}	0.40	fcc	0.4139	-	-	-	-	-	-	-	-
(Mo ₂ N)	0.54 (1200 K)		0.4162	9.48 ^a	Gray	17 ^b	-	-	9.3	-	~5.08
MoN	-	hex	^a 0.5745 ^c 0.6122	8.1 9.1 ^c	Gray	-	-	-	-	-	15.1

^aNitrogen-rich phase boundary depends on nitrogen pressure. ^bExact composition unknown, probably close to 2:1 (CrN_{1-x}, MoN_{1-x}) or 1:1 (all others) stoichiometry. ^cX-ray density. ^dDecomposes. ^eCalculated. ^fNot superconducting. ^gExact composition unknown.

TABLE 3

Conclusion

In addition to the TiN used in the embodiments, other metal nitrides can be used as conductive nitride material in the present invention. For example, Table 3 lists a number of nitrides which could be used as anode material in OLEDs. In particular, ZrN is a refractory
5 metallic conductor, with similar characteristics to TiN.

The present invention provides monochromatic and multicolor light emitting devices with high brightness and efficiency. Those with skill in the art may recognize various modifications to the embodiments of the invention described and illustrated herein. Such modifications are meant to be covered by the spirit and scope of the appended claims.

What is Claimed is:

1. An organic light emitting device (OLED), comprising a conductive nitride electrode.
2. The OLED of claim 1, wherein the conductive nitride electrode comprises conductive nitride material selected from the group consisting of TiN, ZrN_{1-x} , HfN_{1-x} , VN_{1-x} , NbN_{1-x} , TaN_{1-x} , CrN, Cr_2N , MoN, Mo_2N , and combinations thereof.
3. The OLED of claim 2, wherein the conductive nitride electrode comprises TiN.
4. An organic light emitting device (OLED), comprising a transparent electrode and a conductive nitride formed on the transparent electrode.
5. The OLED of claim 4, wherein the conductive nitride comprises conductive nitride material selected from the group consisting of TiN, ZrN_{1-x} , HfN_{1-x} , VN_{1-x} , NbN_{1-x} , TaN_{1-x} , CrN, Cr_2N , MoN, Mo_2N , and combinations thereof.
6. The OLED of claim 5, wherein the conductive nitride comprises TiN.
7. The OLED of claim 5, wherein the transparent electrode comprises indium tin oxide (ITO).
8. The OLED of claim 7, wherein the conductive nitride comprises TiN.

9. An organic light emitting device (OLED), comprising:

a substrate;

a first conductive nitride electrode formed on a top surface of the substrate;

an organic film formed on the conductive nitride; and

5 an second electrode formed on the organic film,

wherein the organic film emits light upon application of a voltage between the first conductive nitride electrode and the second electrode.

10. The OLED of claim 9, wherein the conductive nitride comprises TiN.

11. The OLED of claim 10, wherein the conductive nitride can act as either an anode or a cathode upon stacking of the OLED with a second OLED.

12. The OLED of claim 10, wherein the electrode layer is transparent.

13. The OLED of claim 10, wherein the TiN thickness ranges from approximately 40-180 Å.

14. The OLED of claim 10, wherein the organic film comprises first and second layers.

15. The OLED of claim 14, wherein the first organic layer is an electron transporting layer, and the second organic layer is electroluminescent and a hole transporting

layer.

16. The OLED of claim 15, wherein the first organic layer comprises 4,4'-Di(phenyl- α -naphthylamino)biphenyl (α -NPD) and the second organic layer comprises aluminum-tris(8-quinoloxide) (Alq₃).

17 The OLED of claim 16, wherein the electrode sheet resistance is approximately less than 400 Ω/\square .

18. The OLED of claim 16, wherein the corrected external quantum efficiency is approximately 0.60% or higher.

19. An organic light emitting device (OLED), comprising:

a substrate;

a first transparent electrode formed on a top surface of the substrate;

a conductive nitride formed on the transparent electrode;

an organic film formed on the conductive nitride; and

a second electrode layer formed on the organic layer,

wherein the organic layer emits light upon application of a voltage between the conductive nitride and first transparent electrode and the second electrode.

20. The OLED of claim 19, wherein the second electrode is transparent.

21. The OLED of claim 19, wherein the first transparent electrode comprises indium tin oxide (ITO).

22. The OLED of claim 19, wherein the conductive nitride comprises TiN.

23. The OLED of claim 22, wherein the TiN thickness ranges from approximately 20 to 50 Å.

24. The OLED of claim 19, wherein the conductive nitride and first transparent electrode can act as either an anode or a cathode upon stacking of the OLED with a second OLED.

25. The OLED of claim 22, wherein the second electrode is transparent.

26. The OLED of claim 22, wherein the first transparent electrode comprises ITO.

27. The OLED of claim 26, wherein the organic film comprises first and second layers.

28. The OLED of claim 27, wherein the first organic layer is an electron transporting layer, and the second organic layer is electroluminescent and a hole transporting layer.

29. The OLED of claim 28, wherein the first organic layer comprises 4,4'-Di(phenyl- α -naphthylamino)biphenyl (α -NPD) and the second organic layer comprises aluminum-tris(8-quinoloxide) (Alq_3).

30. The OLED of claim 29, wherein the sheet resistance ranges from approximately 75 to 85 Ω/\square .

31. The OLED of claim 29, wherein the quantum efficiencies range from approximately 0.18 to 0.43%.

32. The OLED of claim 3, wherein the OLED structure is selected from the group consisting of single layer polymer, multi-layer polymer, single heterostructure, and double heterostructure.

33. The OLED of claim 32, wherein the OLED further comprises a transparent cathode.

34. The OLED of claim 33, wherein the transparent cathode comprises a layer of ITO and a layer of metal or metal alloy.

35. An organic light emitting device (OLED), comprising:
a substrate;
a first electrically conductive nitride material formed over the substrate;

- 5 a first organic emissive structure formed over the electrically conductive nitride material;
- a second electrically conductive material formed over the first organic emissive structure;
- further wherein the first and second organic emissive structures independently emit
- 10 light when energized.

36. The OLED of claim 35, wherein the electrically conductive nitride material comprises material selected from the group consisting of TiN, ZrN_{1-x} , HfN_{1-x} , VN_{1-x} , NbN_{1-x} , TaN_{1-x} , CrN, Cr_2N , MoN, Mo_2N , and combinations thereof.

37. The OLED of claim 36, wherein the electrically conductive nitride material comprises TiN.

38. The OLED of 37, wherein the TiN is substantially transparent.

39. The OLED of claim 37, wherein the second electrically conductive material is substantially transparent.

40. The OLED of claim 39, wherein the second electrically conductive material comprises Mg-Ag.

41. The OLED of claim 40, wherein the TiN is opaque.

42. The OLED of claim 38, wherein the second electrically conductive material is substantially transparent.

43. The OLED of claim 37, further comprising:

a second electrically conductive nitride material formed over the substrate;

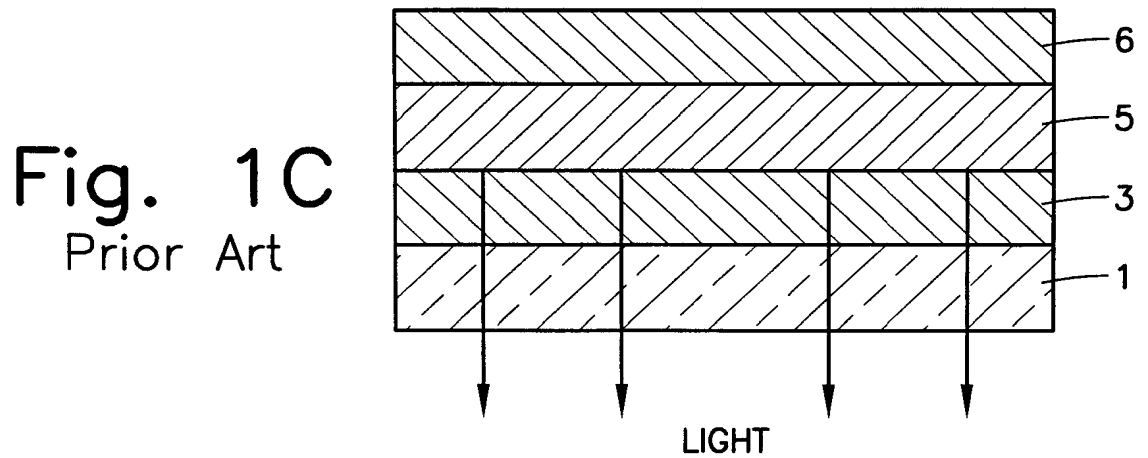
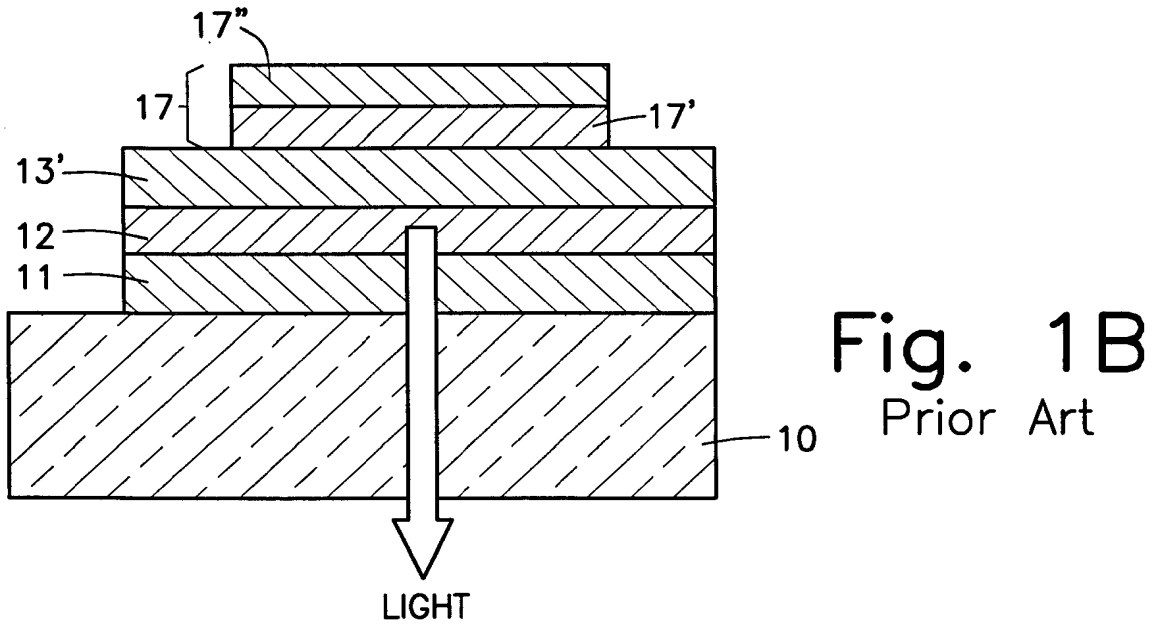
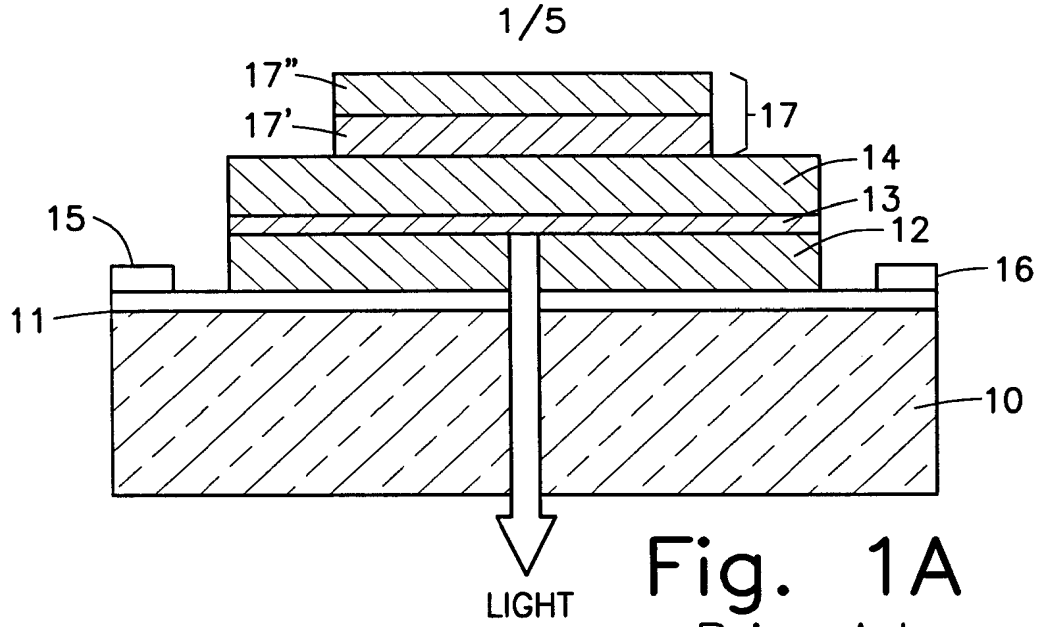
a second organic emissive structure formed over the second electrically conductive nitride material;

5 a third electrically conductive material formed over the second organic emissive structure.

44. The OLED of claim 35, wherein the OLED structure is selected from the group consisting of single layer polymer and multi-layer polymer OLEDs.

45. The OLED of claim 35, wherein the OLED structure is selected from the group consisting of single heterostructure and double heterostructure OLEDs.

46. The OLED of claim 35, further comprising a first transparent electrically conductive material formed over the substrate and under the first electrically conductive nitride material.



2/5

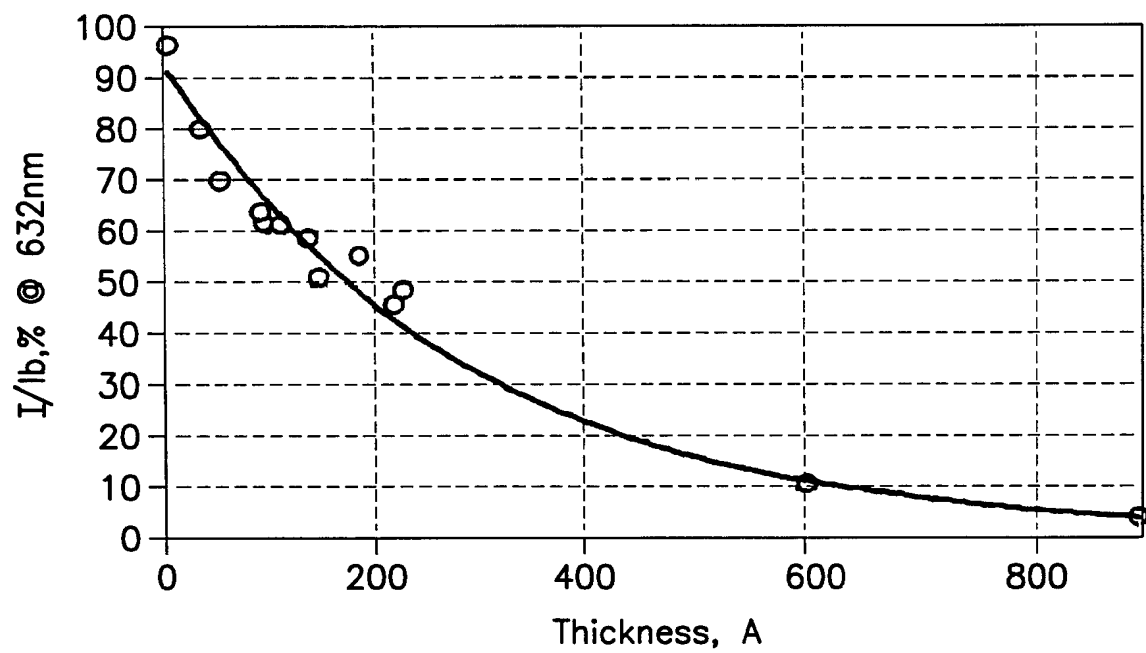


Fig. 2

3/5

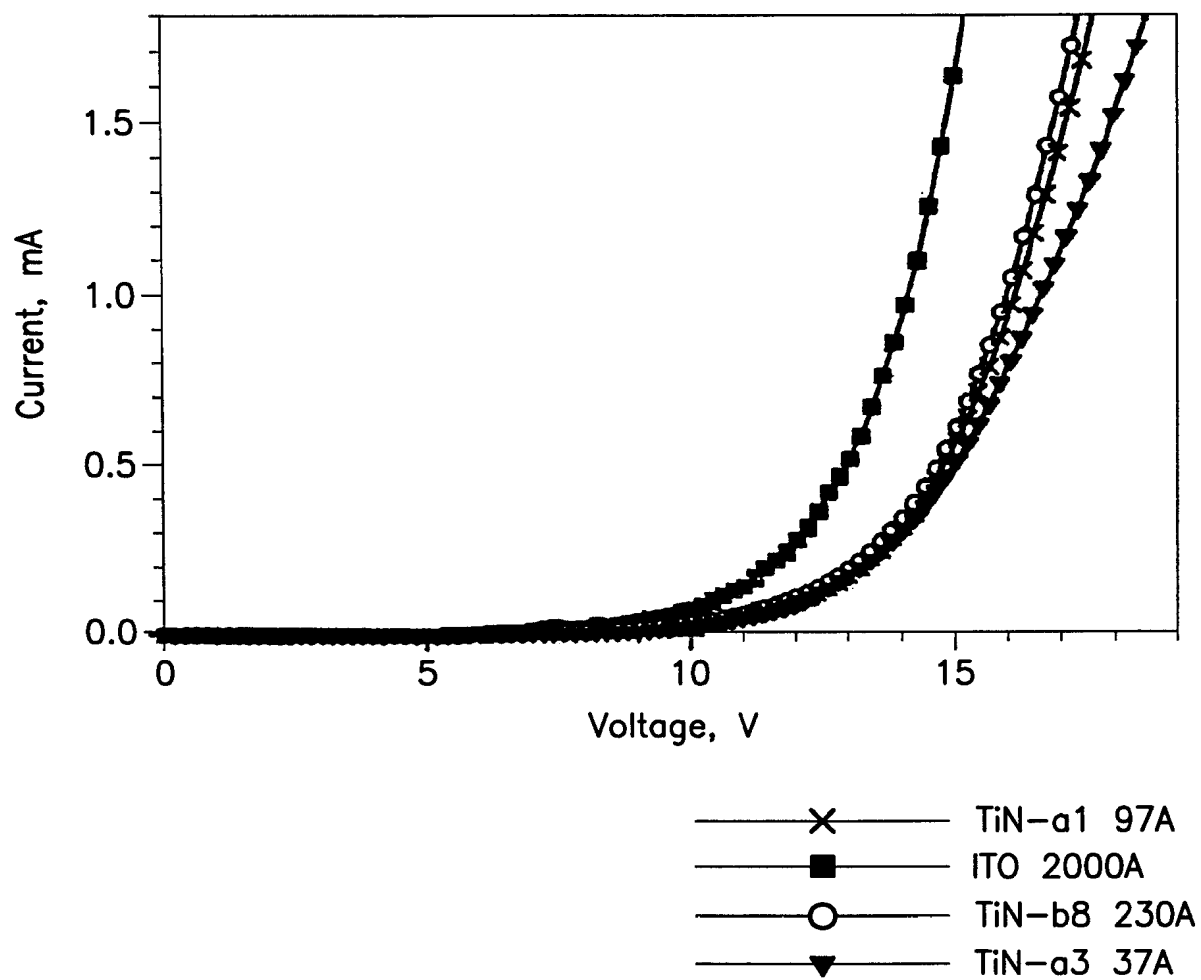


Fig. 3

4/5

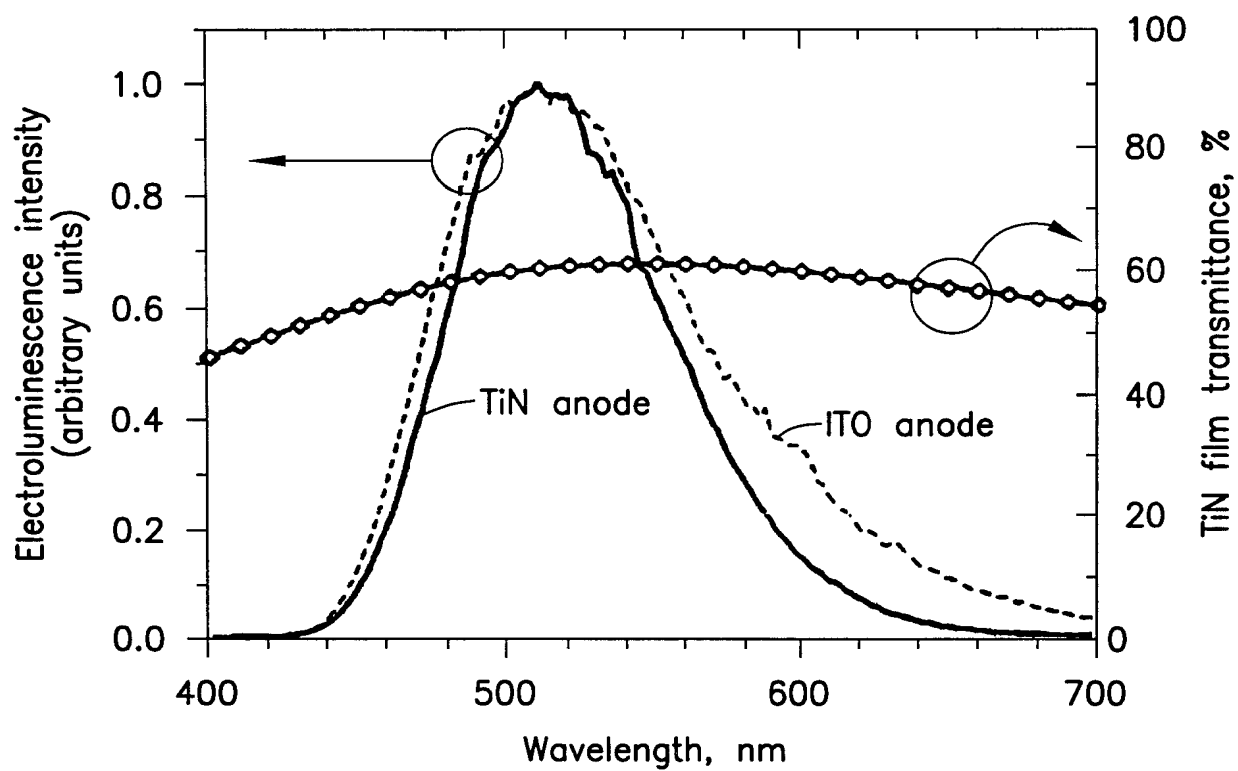


Fig. 4

5/5

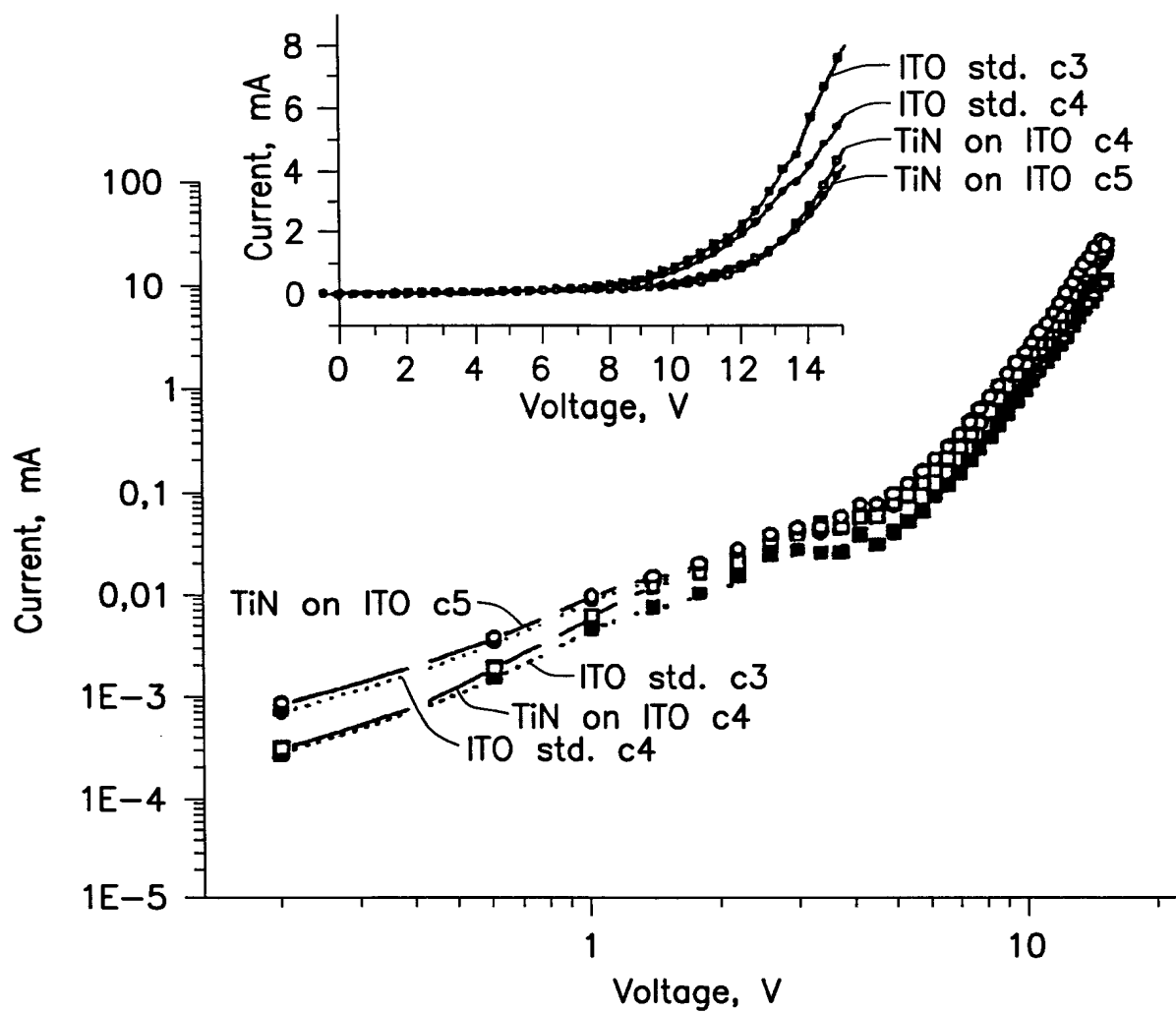


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/12737

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B32B 19/00; H01J 1/62

US CL :313/498, 503, 505, 506; 428/689, 690, 694NF

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 313/498, 503, 505, 506; 428/689, 690, 694NF

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST, searched terms: organic light emitting, nitride, substrate, electrode

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,969,474 A (ARAI) 19 OCTOBER 1999 (19.10.1999), see figures 1-2; column 1, lines 6-18; column 3, lines 19-50.	1-46
X,P	US 5,952,778 A (HASKAL ET AL.) 14 SEPTEMBER 1999 (14.09.1999), see figure 1; column 1, lines 55-60; column 2, lines 2-33; column 3, lines 11-30.	1-46
X,P	US 5,981,092 A (ARAI ET AL.) 09 NOVEMBER 1999 (09.11.1999), see figures 1-2; column 1, lines 12-30; column 4, lines 4-42; column 5, lines 40-65.	1-46
A	US 5,757,026 A (FORREST ET AL.) 26 MAY 1998 (26.05.1998), see figures 1A-2C.	1-46



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

07 JULY 2000

Date of mailing of the international search report

15 AUG 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

THUY VINH TRAN

Telephone No. (703) 305-0012

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US00/12737**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,294,870 A (TANG ET AL.) 15 MARCH 1994 (15.03.1994), see figures 1-7	1-46